(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : 0 594 341 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number : 93308135.8

(22) Date of filing : 12.10.93

(51) Int. Cl.[5] : C07C 15/44, C09K 15/20, C07C 15/46, C07C 7/20, C07B 63/04

(30) Priority : 21.10.92 US 964321
08.09.93 US 118075

(43) Date of publication of application :
27.04.94 Bulletin 94/17

(84) Designated Contracting States :
AT BE DE ES FR GB IT NL PT

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(54) Compositions and methods for inhibiting vinyl aromatic monomer polymerization.

(57) Methods and compositions are provided for inhibiting the polymerization of vinyl aromatic monomers under distillation conditions. The compositions comprise a combination of a phenylenediamine compound and a hydroxylamine compound.

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The present invention relates to compositions and methods for inhibiting the undesirable polymerization of vinyl aromatics.

Polystyrene is a thermoplastic with many desirable characteristics. It is clear. transparent, readily colored and easily fabricated. The family of styrene polymers includes polystyrene itself, copolymers of styrene with other vinyl monomers, polymers of derivatives of styrene and mixtures of polystyrene and styrene-containing copolymers with elastomers. Pure polystyrene is glass-like, transparent, hard, and rather brittle.

ABS (acrylonitrile. butadiene, styrene) and SAN (styrene, acrylonitrile) resins have enjoyed tremendous commercial popularity for many years as durable, temperature and solvent resistant elastomers. On the other hand, styrene plastics are commonly used for packaging, including foams and films, coatings, in appliance fabrication, for housewares and toys, lighting fixtures and in construction materials.

Common industrial methods for producing vinyl aromatic monomers, such as styrene, include a variety of purification processes, the most common one being distillation. It is well known that vinyl aromatic monomers readily polymerize when heated and that the rate of polymerization increases rapidly as the temperature increases. Thermal polymerization during distillation results not only in loss of product, but it could render the finished monomer unsuitable for using without further treatment.

To prevent polymerization of vinyl aromatic monomers under distillation conditions various inhibitor compositions have been employed. Unfortunately, although several compounds are effective against vinyl aromatic monomer polymerization under storage conditions, only some of these compounds have proved to be effective against polymerization under distillation conditions.

The present invention relates to compositions and methods for inhibiting polymerization of vinyl aromatic monomers during processes such as distillation of the vinyl aromatic monomer.

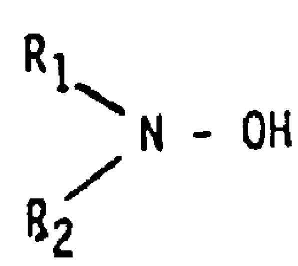
The composition comprises a mixture of a phenylenediamine compound and a hydroxylamine compound in a suitable solvent. This synergistic combination provides an effective method for inhibiting vinyl aromatic polymerization and does not require air to function.

The compounds generally used commercially to prevent polymerization of vinyl aromatic monomers are of the dinitrophenolic type. For example, U.S. 4,105,506, Watson et al., teaches the use of 2,6-dinitro-p-cresol as polymerization inhibitor of vinyl aromatic compounds. U.S. 4,466,905, Butler et al., teaches that 2,6-dinitro-p-cresol and p-phenylenediamines will inhibit polymerization in the distillation column if oxygen is present. U.S. 4,774,374 Abruscato et al., teaches compositions and processes for inhibiting the polymerization of a vinyl aromatic compound employing an oxygenated species formed by the reaction of oxygen and a N-aryl-N'-alkyl-p-phenylenediamine. U.S. 4,720,566 Martin, teaches methods and compositions for inhibiting polymerization of acrylonitrile in the quench tower, no oxygen excluded, using a hydroxylamine compound and a phenyl p-phenylenediamine compound.

While these inventions may inhibit vinyl aromatic monomer polymerization, it would be advantageous to possess polymerization inhibitors that avoid the use of highly toxic compounds such dinitrophenols. It would also be advantageous that the inhibitor does not require air, or oxygen, to function.

The present invention relates to compositions and methods for inhibiting the polymerization of vinyl aromatic monomer comprising a combination of a phenylenediamine compound and a hydroxylamine compound.

The hydroxylamines useful in this invention have the formula

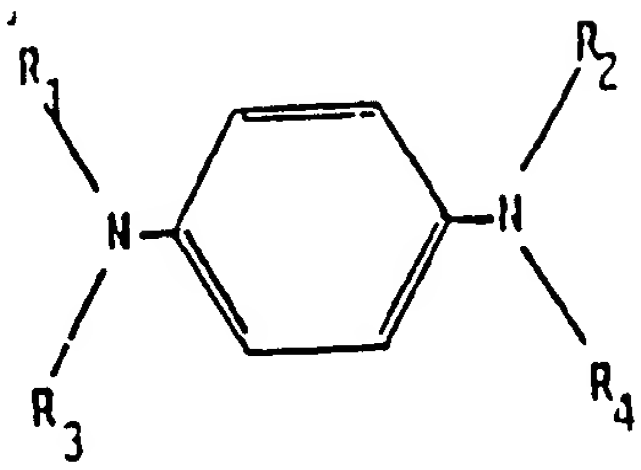


wherein R_1 and R_2 are the same or different and are hydrogen, hydroxyalkyl, alkoxyalkyl, alkyl, aryl, alkaryl or aralkyl groups.

Examples of suitable hydroxylamines include:
hydroxylamine, N-methylhydroxylamine, N,N-dimethylhydroxylamine, N-ethylhydroxylamine, N,N-diethylhydroxylamine, N-(2-hydroxybutyl)hydroxylamine, N-(2-hydroxyethyl)hydroxylamine, N-(2-hydroxypropyl)hydroxylamine, N,N-di-n-propylhydroxylamine, N,N-di-n-butylhydroxylamine, N,N-diphenylhydroxylamine, N-benzylhydroxylamine, N,N-bis(ethylbenzyl)hydroxylamine, N,N-bis-(m-ethylbenzyl)hydroxylamine, N,N-bis-(p-ethylbenzyl)hydroxylamine, or mixtures thereof. Preferably, the hydroxylamine is N,N-bis(hydroxypropyl)hydroxylamine, also called hydroxypropylhydroxylamine (HPHA).

The phenylenediamine component of the inhibitor mixtures of this invention include phenylenediamine and derivatives thereof having at least one N-H group. It is thought that o-phenylenediamine or derivatives thereof having at least one N-H group are suitable in accordance with the instant invention. However, the preferred

phenylenediamine is p-phenylenediamine having the formula



wherein R_1, R_2, R_3, and R_4 are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl groups with the proviso that at least one of R_1, R_2, R_3, or R_4 is hydrogen, more preferably the alkyl, aryl, alkaryl, and aralkyl groups have one to about twenty carbon atoms. The alkyl, aryl alkaryl, and aralkyl groups may be straight or branched-chain groups. Exemplary p-phenylene-diamines include p-phenylenediamine wherein R1, R2, R3, and R4 are hydrogen; N-phenyl-N'-alkyl-p-phenylenediamines such as, N-phenyl-N'-methyl-p-phenylenediamine, N-phenyl-N'-ethyl-p-phenylenediamine, N-phenyl-N'-propyl-p-phenylenediamine, N-phenyl-N'-isopropyl-p-phenylenediamine, N-phenyl-N'-n-butyl-p-phenylenediamine, N-phenyl-N'-isobutyl-p-phenylenediamine, N-phenyl-N'-sec-butyl-p-phenylenediamine, N-phenyl-N'-tert-butyl-p-phenylenediamine, N-phenyl-N'-n-pentyl-p-phenylenediamine, N-phenyl-N'-n-hexyl-p-phenylenediamine, N-phenyl-N'-(1-methylhexyl)-p-phenylenediamine, N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine, N-phenyl-N'-(1,4-dimethylpentyl)-p-phenylenediamine; N-phenyl-N',N'-dialkyl-p-phenylenediamines, such as N-phenyl-N',N'-dimethyl-p-phenylenediamine, N-phenyl-N',N'-diethyl-p-phenylenediamine, N-phenyl-N',N'-di-n-butyl-p-phenylenediamine, N-phenyl-N',N'-di-sec-butyl-p-phenylenediamine, N-phenyl-N'-methyl-N'-ethyl-p-phenylenediamine; N,N-dialkyl-p-phenylenediamines such as N,N-dimethyl-p-phenylenediamine and N,N'-diethyl-p-phenylenediamine; N,N'-dialkyl-p-phenylenediamines such as N,N'-di-isopropyl-p-phenylenediamines; N,N'-diaryl-p-phenylenediamines such as N,N'-diphenyl-p-phenylenediamine; N,N,N'-trialkyl-p-phenylenediamines such as N,N,N'-trimethyl-p-phenylenediamine, N,N,N'-triethyl-p-phenylenediamine. Preferably, the p-phenylenediamine is selected from the group consisting of N-phenyl-N'-(1-3-dimethylbutyl)-p-phenylenediamine and N-phenyl-N'-(1,3-dimethylpentyl)-p-phenylenediamine.

The compositions of the instant invention prove surprisingly effective in vinyl aromatic monomer that are substantially oxygen-free. By relatively oxygen-free, it is meant that little to no oxygen is dissolved in the vinyl aromatic monomer.

The total amount of phenylenediamine compound and hydroxyl-amine compound used in the methods of the present invention is that amount which is sufficient to effect inhibition of polymerization and will, of course, vary according to the conditions under which the vinyl aromatic monomer is being exposed to hot temperatures. At higher processing temperatures, large amounts of the polymerization inhibiting treatment are generally required.

Preferably, the total amount of the combined treatment (phenylenediamine compound and hyroxylamine compound) is from about 1 part per million to about 10,000 parts per million parts combined treatment based on the weight of the vinyl aromatic monomer. Most preferably, the total amount of the combined treatment is from about 5 parts per million to about 500 parts per million based on the weight of the vinyl aromatic monomer. The weight ratio of phenylenediamine to hydroxylamine is preferably from about 9:1 to about 1:9.

The phenylenediamine compound and hydroxylamine compound can be added to the vinyl aromatic monomer by any conventional method. The components can be added separately or as a combination containing both components. It is preferred to add composition as a single treatment composition comprising both of the active vinyl aromatic monomer polymerization inhibitors.

Accordingly, it is therefore possible to produce a more effective vinyl aromatic polymerization inhibition treatment than is obtainable by use of either individual ingredient alone when measured at comparable treatment levels. Because of the enhanced polymerization activity of the combination, the concentration of each of the ingredients may be lowered and the total quantity of the polymerization inhibitor required for an effective treatment at elevated temperatures may be reduced.

The composition may be added to the vinyl aromatic monomer as either a dispersion or a solution using a suitable liquid carrier dispersing medium which is compatible with the vinyl aromatic.

The preferred inventive embodiment employs N,N'-di-sec-butyl p-phenylenediamine (PDA) and bis-N-N'(hydroxypropyl) hydroxylamine (HPHA). Optimal dosage rates are about 5 parts per million to about 500 parts per million of the combination per one million parts of the styrene monomer for which polymerization inhibition

is desired.

Examples

The invention will now be further described with reference to a number of specific examples which are to be regarded solely as illustrative, and not as restricting the scope of the invention.

Freshly distilled styrene (70 ml) with an appropriate amount of inhibitor was placed in a 100 ml flask. The solution was purged with argon for 30 minutes and the liquid was heated to 100°C or 120°C in an oil bath.

Argon spurging continued throughout the test. Samples were removed from the flask every half hour or 15 minutes and poured into 50 ml of methanol. The resulting polymer was filtered, dried overnight and then weighed. Results of this testing are reported in Tables I and II.

TABLE I

Styrene Reflux under Argon* at 100°C
Milligrams of Polymer vs. Time

Time (min)	DNPC # 50 ppm mg polymer/5mL	PDA/HPHA 25/25 ppm mg polymer/5mL
30	1	0
60	2	0
90	3	0
120	6	0

* less than 0.5 ppm of O_2

#2,6-Dinitro-p-cresol

TABLE II

Styrene Reflux under Argon at 120°C

Time (min)	DNOC #100 ppm mg polymer/5mL	PDA/HPHA 25/25 ppm mg polymer/5mL
15	1	0
30	2	0
45	5	0
60	10	1

#2,6-Dinitro-o-cresol

The same experiment as described above was carried out in the presence of air instead of argon. A styrene sample containing 100 ppm of PDA/HPHA was heated for six hours with no signs of polymerization. This data indicate that, in the presence of air, an even greater synergism exists between the two components.

As seen in Tables I - II, this combination proved more effective than known styrene polymerization inhibitors.

In another test, freshly distilled styrene (5 ml) with the appropriate amount of treatment was placed in a test tube. The test tube was capped with a septum and the solution was purged for 3 minutes with argon using two needles. The test tube was then placed for 2 hours in an oil bath heated at 100°C. At the end of this time, the styrene solution was cooled to room temperature and poured into 50 ml of methanol. The resulting polymer was filtered, dried, and reweighed. These results are shown in Table III.

TABLE III

Treatment	Dose (ppm)	Polymer mg/5mL
Blank	-----	174
PDA	100	33
PDA	50	114
PDA	25	130
HPHA	100	70
HPHA	50	105
HPHA	25	141
PDA/HPHA	50/50	22
PDA/HPHA	25/25	60

The data in Table III clearly shows there is a synergistic effect between the two components of this invention.

While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications will be oovious to those skilled in the art. The appended claims generally should be construed to cover all such obvious forms and modification which are within the true spirit and scope of the present invention.

Claims

1. A vinyl aromatic polymerization inhibiting composition comprising a phenylenediamine compound and a hydroxylamine compound.

2. A composition as claimed in claim 1, wherein said phenylenediamine compound is N,N'-di-sec-butyl-p-phenylene diamine, N-phenyl-N'-(1-3-dimethylbutyl)-p-phenylenediamine or N-phenyl-N'- (1,3-dimethylpentyl)-p-phenylenediamine.

3. A composition as claimed in claim 1 or 2, wherein said hydroxylamine compound is bis-N-N' (hydroxypropyl) hydroxylamine.

4. A composition as claimed in any one of the preceding claims, wherein the weight ratio of said phenylenediamine compound to said hydroxylamine compound ranges from about 9:1 to about 1:9.

5. A composition as claimed in any one of the preceding claims, wherein said composition is contained in a liquid carrier.

6. A composition as claimed in any one of claims 1 to 5, together with a vinyl aromatic monomer.

7. A method for inhibiting the polymerization of vinyl aromatic compounds under distillation conditions comprising adding to said vinyl aromatic compound a combination of a phenylenediamine compound and a hydroxylamine compound.

8. A method as claimed in claim 7, wherein said phenylenediamine compound is N,N'-di-sec-butyl p-phenylenediamine, N-phenyl-N'-(1-3-dimethylbutyl)-p-phenylenediamine or N-phenyl-N'- (1,3-dimethylpentyl)-p-phenylenediamine.

9. A method as claimed in claim 7 or 8, wherein said hydroxylamine compound is bis-N, N'(hydroxypropyl) hydroxylamine.

10. A method as claimed in any one of claims 7 to 9, wherein the weight ratio of said phenylenediamine com-

pound and said hydroxylamine compound ranges from 9:1 to about 1:9.

11. A method as claimed in any one of claims 7 to 10, wherein the amount of said phenylenediamine compound and said hydroxylamine compound added, collectively to the styrene monomer is from about 1 part per million to about 10,000 parts per million parts of said styrene.

12. A method as claimed in any of claims 7 to 11, wherein said combination is added to said vinyl aromatic compound in a liquid carrier solvent.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 30 8135

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
D,A	US-A-4 720 566 (J MARTIN ET AL) * claims *	1,7	C07C15/44 C09K15/20 C07C15/46 C07C7/20 C07B63/04
D,A	US-A-4 466 905 (J BUTLER ET AL) * claims *	1,7	
D,A	US-A-4 105 506 (J WATSON) * claims *	1,7	
A	EP-A-0 240 297 (BETZ EUROPE) * claims *	1,7	
A	EP-A-0 266 906 (BETZ EUROPE) * claims *	1,7	
A	CHEMICAL ABSTRACTS, vol. 108, no. 24, 13 June 1988, Columbus, Ohio, US; abstract no. 205239, page 10 ;column 1 ; * abstract * & CS-A-246 182 (V HAVLU ET AL)	1,7	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 February 1994	Heywood, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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